Inelastic processes of light scattering in alkali-metal vapor. Molecular fluorescence

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(Submitted August 20, 1976)
Zh. Eksp. Teor. Fiz. **72**, 1738–1748 (May 1977)

Results are presented of an experimental investigation of two types of processes in the gas phase: a) $Cs+Cs^*\rightarrow Cs_2+\hbar\omega$ and b) $Cs+Cs+\hbar\omega_1\rightarrow Cs_2^*\rightarrow Cs_2+\hbar\omega_2$; $Rb+Rb+\hbar\omega_1\rightarrow Rb_2^*\rightarrow Rb_2+\hbar\omega_2$. The efficiency of these processes is investigated as a function of the exciting-radiation, power and wavelength as well as of the pressure of the monatomic vapor in the range 0.1–10 Torr. A large efficiency of production of molecules from atoms is observed (5% of the total number of atoms). The binding of the atoms into molecules in a radiation field is interpreted as free-bound transitions between the electron-translational and electron-vibrational molecular states of the pair of colliding atoms. The main contribution to the observed processes is made by atoms that collide at velocities and impact distances that ensure a prolonged stay of the atoms near each other (the orbiting state). The appearance of orbiting states in the absorption spectrum of Rb and Cs vapor is noted.

PACS numbers: 33.50.Dq

1. The influence of the radiation field on the dynamics of the collision of atoms was discussed by us in an earlier article,[1] where we reported observation of inelastic scattering of light, in alkali-metal vapor accompanied by a change in the energy of the relative translational motion of the atoms. These processes are the result of an instantaneous change of the potential of the interatomic interaction when a light quantum is absorbed by the colliding atoms. The associated change in the character of the interaction of the colliding particles can lead, under definite conditions, to a transition of the atoms in the radiation field into a bound molecular state. The present communication is devoted to an investigation of such processes.

2. Two of the possible processes that result in a transition of a pair of colliding atoms from a state of infinite motion into a bound state are illustrated in Fig 1. Both processes are realized when the atoms come so close together that they fall in the range of action of the molecular forces. The first of these processes (Fig. 1a) occurs when a photon is absorbed by two colliding unexcited atoms and a molecule is produced in the excited state.

The second process (Fig. 1b) corresponds to collision of an excited and an unexcited atom with simultaneous spontaneous emission of a photon, which leads to a transition of the atoms to a bound molecular ground state ("recombination with irradiation"[2]). Both processes can be described as photoreactions of the type

$$A+A+\hbar\omega_1\rightarrow A_2^*\rightarrow A_2+\hbar\omega_2,$$
$$A+A^*\rightarrow A_2+\hbar\omega.$$

The observation and investigation of these phenomena under laboratory conditions entails a number of difficulties. First, the investigated processes have low efficiency because of the strong adiabaticity of the free-bound transitions: the probability of these transitions is low to the extent that the Franck-Condon overlap integral of the wave functions of the particle motion in the free and bound states is small. Second, for a reliable registration of such processes it is necessary that the multiparticle collisions (triple, etc.) be rare in comparison with binary collisions, a situation realized in rarefied media. But since the time during which the distance between the atoms is small (on the order of several angstroms in the quasimolecule states) is of the order of 10^{-12} sec and is small both in comparison with the time between collisions (10^{-6}–10^{-7} sec at a pressure of 1 Torr) and with the lifetime of the excited atom (10^{-8} sec for allowed transitions), to use intense radiation fluxes it is necessary to produce enough bound pairs of atoms to be registered.

3. The investigated object of alkali-metal vapor (Rb and Cs). Saturated vapor of these metals is a two-com-

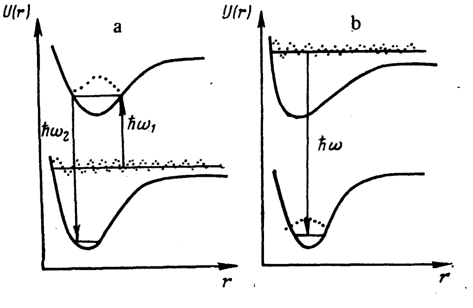

FIG. 1. Binding of two colliding atoms into a molecular state: a) in collisions of unexcited atoms; b) in the collision of an unexcited atom with an excited one.

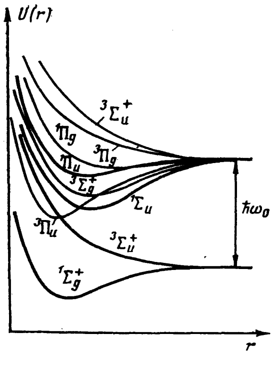

FIG. 2. Approximate level scheme of alkali-metal atoms.

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ponent equilibrium mixture of atoms and molecules with a concentration ratio $N_m/N_a \sim 10^{-3}-10^{-2}$ and $N_a \sim 10^{16}-10^{17}$ cm^{-3} at $T \sim 300-380$ °C. An approximate level scheme of the alkali metals is shown in Fig. 2,[5] and the absorption spectra of rubidium and cesium vapor can be found, for example, in[1,2]; these spectra constitute two molecular absorption bands connected with the transitions $^1\Sigma_g^+ - {}^1\Sigma_u^+$ and $^1\Sigma_g^+ - {}^1\Pi_u$ and located respectively on the long-wave and short-wave sides of the atomic D lines of the principal doublet.

4. The first process—a transition of a pair of colliding unexcited atoms into a bound excited molecular state—was investigated by us following excitation of Rb and Cs vapors by neodymium-laser radiation ($\lambda = 1060$ nm). We observed in this case molecular fluorescence in the region of the short-wave bands $^1\Pi_u - {}^1\Sigma_g^+$ of both Cs_2 and Rb_2. The onset of fluorescence in this region of the spectrum cannot be ascribed to excitation of the molecules into the $^1\Pi_u$ state from the ground $^1\Sigma_g^+$ state as a result of direct transitions under the influence of the incident laser radiation, since the quantum energy of this radiation was much lower than the minimum necessary for such transitions. The energy deficit, determined from the data of[2,3] was ~ 400 cm^{-1} for Cs_2 and ~ 1200 cm^{-1} for Rb_2.

A possible mechanism of excitation of the molecules into the $^1\Pi_u$ state might be the process of resonance transfer of excitation energy from atoms of molecules,1) inasmuch as at the employed laser intensities there were many excited atoms in the system (the mechanism of nonresonant excitation of atoms discussed by us earlier[1]). However, the observed large difference between the durations of the molecular and atomic fluorescence cannot explain the observed molecular fluorescence as being due to such an excitation transfer. The duration of the molecular fluorescence did not exceed 2×10^{-7} sec (the time resolution of the employed apparatus) and was smaller by at least one order of magnitude than the duration of the atomic fluorescence (2×10^{-6} sec). The latter was determined by the processes of capture of the spontaneous radiation of the atoms at the D-line wavelengths.

A second conceivable mechanism, the transfer of excitation from the excited $^1\Sigma_u^+$ state to the $^1\Pi_u$ state following collision of excited molecules with unexcited atoms, cannot be the main cause of the excitation of the $^1\Pi_u$ state, owing to the difference of the dependences of the fluorescence intensity of the $^1\Sigma_u^+ - {}^1\Sigma_g^+$ and $^1\Pi_u - {}^1\Sigma_g^+$ bands on the excitation intensity I_0. The fluorescence intensity of the long-wave band $^1\Sigma_u^+ - {}^1\Sigma_g^+$ increases in proportion to the square root I_0 (at $I_0 > 10^3$ W/cm^2), whereas the fluorescence intensity in the vicinity of the $^1\Pi_u - {}^1\Sigma_g^+$ band was proportional to I_0.2)

Finally, it was established that the intensity of the observed molecular fluorescence depends linearly on the intensity of the exciting radiation (up to an intensity ~ 10^8 W/cm^2) and is proportional to the square of the concentration of the atoms.

The aggregate of the described results allows us to conclude that the observed fluorescence is due to spontaneous decay of the excited molecules that are produced when two colliding atoms go over to the excited state when they absorb a laser-emission quantum. As a result of the spontaneous transition, stable molecules are produced in the $^1\Sigma_g^+$ ground state.

It was further established that the dependence of the emission intensity of the Cs vapor in the region of the short-wave band on the excitation intensity I_0 deviates from linearity at $I_0 > 10^8$ W/cm^2 (Fig. 3). There can be two possible causes of this deviation: 1) saturation of the free-bound transitions by the exciting radiation, and 2) competition in the depletion of the excited molecular state between the spontaneous transitions into the bound $^1\Sigma_g^+$ state and stimulated transitions into the continuum of the same state. We note that the registered radiation is connected only with the spontaneous transitions.

We attribute the observed nonlinearity to the second cause, inasmuch as at the atom concentrations realized under the conditions of our experiments the probability, per unit time, of binding of atoms by radiation is much lower than the corresponding probability of disintegration, by the same radiation, of the produced excited molecules as a result of induced transitions to the initial states of the fly by atoms (Fig. 1a). The radiation intensity at which the probabilities of the processes that deplete the excited molecular state become equalized is determined by the relation $\gamma = W$, where γ^{-1} is the radiative spontaneous lifetime of the excited state, ~ 2×10^{-8} sec, and W is the probability per unit time of disintegration of an excited molecule via induced transitions. The relation $\gamma = W$, rewritten in the form $\gamma = cN\sigma$, where N is the photon flux density at the intensity $I_0 = 10^8$ W/cm^2, enables us to determine the photodecay cross section σ, which turns out to be $\approx 3 \times 10^{-20}$ cm^2 and is of the order of the photodissociation cross sections. This result is somewhat unexpected, if it is recognized that the vapor fluorescence in the region of the short-wave molecular band is due to direct radiative excitation of the $^1\Pi_u$ state, since this process is adiabatically strongly forbidden (the Massey parameter for this transition is $\xi_M \sim 50$3)). It is more natural to attribute the excitation of this fluorescence to transitions from the continuum of the ground $^1\Sigma_g^+$ state to high-lying vibrational-rotational levels of the excited $^1\Sigma_u^+$ state (this transition is allowed in accordance with the Franck-Condon principle). Inasmuch as these levels lie near the bottom of the potential curve of the $^1\Pi_u$ state (Fig. 2), the spontaneous transitions $^1\Sigma_u^+ - {}^1\Sigma_g^+$ lead to the appearance of fluorescence with wavelengths that lie in the region of the short-wave molecular band.

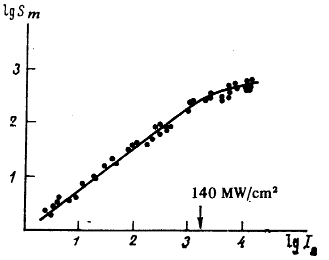

FIG. 3. Dependence of the fluorescence intensity of cesium vapor in the $^1\Pi_u - {}^1\Sigma_g^+$ band on the excitation intensity.

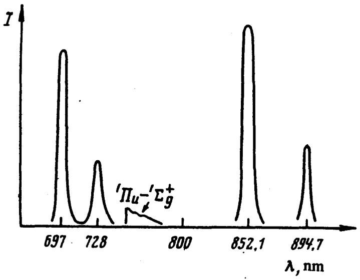

FIG. 4. Emission spectrum of cesium vapor excited to an atomic line (the intensities of the atomic lines are decreased by a factor of 20).

5. The second binding process—recombination of atoms with radiation—was investigated in Cs vapor ($N_a \sim 10^{15}-10^{17}$ cm^{-3}) by observing the fluorescence following excitation of the vapor by a tunable organic-dye laser with a power density $I_0 \sim 10^6$ W/cm^2, a pulse duration $\sim 2\times10^{-8}$ sec, and an emission-spectrum width ~ 2 cm^{-1}. When Cs atoms were excited in the vicinity of the D_2 line ($\lambda = 825.1$ nm), we observed simultaneously with the atomic emission also the molecular bands $^1\Pi_u - ^1\Sigma_g^+$ and $^1\Sigma_u^+ - ^1\Sigma_g^+$. Their presence is due to the direct excitation of the corresponding transitions by the laser radiation. This is confirmed both by the linear dependence of the intensity I_M of the molecular fluorescence on the concentration of the molecules, and by the character of its dependence on the excitation power ($I_m \sim I_0$) at low intensities and $I_m \sim \sqrt{I_0}$ at a power density $I_0 > 10^5$ W/cm^2[4]). In addition, the fluorescence intensity was practically independent of the frequency detuning of the exciting radiation relative to the frequency of the D_2 line of Cs in a detuning range $\leqslant 200$ cm^{-1}. Finally, the molecular-fluorescence pulse duration was determined by the temporal resolution of the recording apparatus [2×10^{-7} sec) and was much shorter than the duration of the fluorescence pulse of the Cs atoms in the D lines (2×10^{-6} sec).4)

Besides the known molecular bands, the fluorescence spectrum revealed two new bands near $\lambda = 697$ and 728 nm, of widths ≈ 10 nm (the fluorescence spectrum of the vapor is shown schematically in Fig. 4). The fluorescence intensity in these bands increased in resonant fashion with decreasing detuning of the excitation frequency relative to the D_2 line, and the kinetics coincided with that of the fluorescence of the atoms in the D lines.5) The distance between the new bands was close to the distance between the D lines of the Cs atoms. The emission intensity of these new bands was proportional to the square of the atom concentration and increased linearly with the number of excited atoms; this number was determined from the atomic-line emission intensity. The integrated fluorescence intensity in the new bands, at a cesium atom concentration 2×10^{17} cm^{-3}, was approximately one order of magnitude larger than the intensity of the molecular emission in the ordinary bands (Fig. 4) and constituted $\sim 5\%$ of the integrated intensity of the atomic fluorescence.

6. The appearance and the singularities in the behavior of the new 697 and 729 nm bands can be qualitatively explained within the framework of the concepts described above concerning the binding of an excited atom colliding with an unexcited one into a bound $^1\Sigma_g^+$ ground state (Fig. 1b). The energy deficit of the scattered and excited emission quanta is supplemented in this case by the loss of energy of the colliding particles, which go over into a bound molecular state that lies below the energy levels of the free atoms.

An unexpected feature was the small width of the observed bands and the high efficiency of the recombination process (according to the measurement data, the recombination cross section was $\approx 10^{-14}$ cm^2). We note that the recombination efficiency measured by determining the ratio of the emission intensities in the new bands and at the wavelengths of the D lines increases substantially because of the capture of the radiation in the atomic lines (under the experimental conditions, the effective lifetime of the excitation of the atoms due to capture increases by approximately 100 times), but even this increase cannot ensure so high an efficiency of the binding process. Both mentioned facts point to the presence in the system of colliding atoms of preferred states, spontaneous transitions from which to the bound $^1\Sigma_g^+$ state are much more probable than the ordinary recombination transitions that occur during a flight time $\sim 10^{-12}$ sec.

The appearance of preferred states in the continuous spectrum corresponding to infinite motions is usually due to the presence of singularities in the phase of the scattering matrix. Such singularities arise only in scattering by potentials having an attraction region, and point to the existence of prolonged quasi-finite motions of the particles next to one another.

In this paper we confine ourselves to examination of the simplest model of such quasi-finite motions, and attribute them to the phenomenon of the classical "orbiting."6) The gist of this phenomenon is the following: when describing the motion of the particles in the field of a central potential $U(r)$, the radial motion can be reduced to one-dimensional with the aid of an effective radial potential $U_l(r)$:

$$U_l(r)=U(r)+M^2/2\mu r^2,$$

where μ is the particle mass; M is the orbital angular momentum ($M=\hbar\sqrt{l(l+1)}$), and l is the orbital quantum number. The effective potentials for a number of values of l are shown schematically in Fig. 5. It is seen from the figure that the atoms whose energies ε_0 and impact parameters l_0 satisfy the condition a)

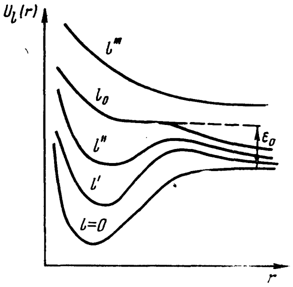

FIG. 5. Forms of the effective molecular potentials for different orbital quantum numbers.

$$U_{l_0}'(r_0)=U_{l_0}''(r_0)=0$$

and the condition b)

$$\varepsilon_0=U_{l_0}(r_0),$$

will execute infinitely prolonged rotation about the center, since the point $r=r_0$ is the stopping point in the case of one-dimensional motion (in Fig. 5, this situation corresponds to the energy ε_0 and the orbital number l_0). The particles whose collision parameters are close to ε_0 and l_0 will stay a limited time near the center and will execute several revolutions. These motions and the corresponding quantum states will henceforth be called orbiting states. It is obvious beforehand that transitions from these states are most probable simply by virtue of the longer stay of the atoms close to one another.

To compare the consequences of the proposed explanation with the experimental data, we have estimated a number of quantities on the basis of an approximation of the molecular terms of the ground (I) and excited (II) states by Morse potentials

$$U^{\mathrm{I,II}}(r)=-D^{\mathrm{I,II}}\{2\exp[-\beta^{\mathrm{I,II}}(r-r_e^{\mathrm{I,II}})]-\exp[-2\beta^{\mathrm{I,II}}(r-r_e^{\mathrm{I,II}})]\},$$

where D is the depth of the potential well, r_0 is the coordinate of the minimum of the potential, β is a characteristic of the width of the potential well and is connected with the frequency ω_0 of the first vibrational transition by the relation

$$\beta=\omega_0(\mu/2D)^{1/2}.$$

The conditions a) and b) make it possible to determine all the necessary characteristics of the orbiting state. In the calculations we chose the following parameters for the molecular potentials of Cs_2[3,5]: $D^{\mathrm{II}}=2140$ cm^{-1}, $\omega_0^{\mathrm{II}}=34$ cm^{-1}, $r_e^{\mathrm{II}}=4\cdot10^{-8}$ cm for the excited $^1\Pi_u$ state and $D^{\mathrm{I}}=3200$ cm^{-1}, $\omega_0^{\mathrm{I}}=42$ cm^{-1}, $r_e^{\mathrm{I}}=5.5\cdot10^{-8}$ cm for the ground $^1\Sigma_g^+$ state. The numerical solution of Eqs. a) and b) for the $^1\Pi_u$ state make it possible to obtain the quantities $r_0=6\cdot10^{-8}$ cm, $l_0=500$, $\varepsilon_0=790$ cm^{-1} and the impact distance $\rho=\hbar l_0/(2\mu\varepsilon_0)^{1/2}=0.6\cdot10^{-7}$ cm. The obtained estimates7) show that an orbiting state sets in for atoms that collide with a relative-motion kinetic energy on the order of thermal ($kT=400$ cm^{-1}) and sufficiently large impact parameters (average distance between atoms $\sim10^{-6}$ cm).

The calculated values of the parameters of the orbiting states were not measured directly, but their values point to a realistic possibility of the manifestation of these states in the investigated system. The quantities that permit a direct comparison with experiment are the position and the width of the spectrum of the recombination-emission band, which were determined from the following considerations.

We note first of all that under conditions of quasiclassical motion the Franck-Condon principle is stringent, and calls for "verticality" of the transitions from one state to another. Further, since the proton carries away a unity angular momentum in the dipole transition, the quantum orbital number l remains practically unchanged on going from the orbiting $^1\Pi_u$ state to the ground $^1\Sigma_g^+$ state, and therefore the energy of the spontaneous-emission quantum is practically independent of l and is determined only by the relation

$$\hbar\omega=U^{\mathrm{II}}(r)-U^{\mathrm{I}}(r).$$

Substituting $r=r_0$ in the corresponding expressions for the potential, we obtain the following values for the wavelengths of the transitions from two (with allowance for the spin-orbit splitting) orbiting states $^1\Pi_u$ to the ground $^1\Sigma_g^+$ state: $\lambda_1=744$ nm and $\lambda_2=713$ nm; in view of the roughness of the assumed approximations, this agrees well with the observed positions of the bands ($\lambda=728$ and 697 nm). We note that at $l\approx l_0$ the effective potential of the ground $^1\Sigma_g^+$ state still remains a binding potential, since the depth and slope of the ground state $^1\Sigma_g^+$ are larger than those of the excited $^1\Pi_u$. The binding follows also from energy considerations, since the energy of the exciting quantum ($\lambda=852.1$ nm) is much less than the energy of the emitted quantum ($\lambda\sim700$ nm).

To estimate the spectral width of the recombination band we shall use a method frequently employed in the calculations of photodissociation spectra.[2,8] In this method the wave functions of the final state are assumed to be δ functions that differ from zero only at the turning points of the classical trajectories. The shape of the fluorescence band is obtained in this method by mapping the contour of the wave function of the initial state on the line that represents the term of the final state. In order to ascertain the form of the wave function in the vicinity of the orbiting point r_0, we expand the function $U_{l_0}^{\mathrm{II}}(r)$ in a series in the vicinity of this point and retain only the first nonvanishing terms:

$$U_{l_0}(\xi)=\varepsilon_0-0.07D\beta^3\xi^3,$$

where $\xi=r-r_0$. For a particle moving with energy ε_0- the radial wave function $R_l(r)=\chi_l(r)/r$ in the vicinity of $\xi=0$ can be determined from the equation

$$\chi_l''+B_l\xi^3\chi_l=0,$$

where $B_l=0.07\cdot2\mu D\beta^3\hbar^{-2}$. A particular solution of this equation is $\chi_l(\xi)=N^{-1}J_{1/5}[\frac{2}{5}(B_l\xi^5)^{1/2}]$, where N is a normalization constant and $J_{1/5}(x)$ is a Bessel function of order 1/5. The function $\chi_l(\xi)$ has in the vicinity of $\xi=0$ a sharp maximum whose width $\Delta\xi$ is determined from the condition $\frac{2}{5}(B_l\Delta\xi^5)^{1/2}\approx1$, which in our case goes over into $\Delta\xi\approx8\cdot10^{-9}$ cm. The width of the fluorescence band is obtained by multiplying the slope of the potential curve of the $^1\Sigma_g^+$ state at the point r_0 by the quantity $\Delta\xi$, and amounts to $U_{l_0}^{\mathrm{I}}(r_0)\Delta\xi=25$ cm^{-1}. The difference between the calculated and the measured (~150 cm^{-1}) values of the widths of the fluorescence bands can be attributed to a band broadening that is inhomogeneous in l and ε and whose value is impossible to calculate at the present time because of the difficulties in estimating the regions of the impact parameters $l\sim l_0$ and energies $\varepsilon\sim\varepsilon_0$ that make the main contribution to the orbiting. For the same reason, it is also impossible to estimate the cross section of the recombination process.

In conclusion, we remark on the fate of the bound pairs of atoms. Since the energy of the produced molecules in the ground $^1\Sigma_g^+$ state corresponds to strongly excited rotational states, while the dimensions of the molecules are large enough, one should expect them to dissociate effectively when they collide with atoms. We have attempted to register the increase of the total number of molecules by determining the change of the molecular absorption after excitation of cesium vapor by radiation from an organic-dye solution laser. Even though we estimated the number of produced molecules at double the number of the initial molecules in the excitation volume, 8) the attempt was unseccessful, possibly because of the competing process of photodecay of the molecules under the influence of the powerful radiation.[9]

7. In the same spectral region ($\lambda = 680-740$ nm) where the two new fluorescence bands of the cesium vapor were registered, we have observed singularities in the vapor absorption spectrum (Fig. 6a). We attribute the two structured bands of width ~10 nm to transitions from the ground $^1\Sigma_g^+$ state to two (with allowance for the spin-orbit splitting) excited orbiting states. A confirmation of this assumption is the fact that both bands appeared in the excitation spectrum of the atomic line, i.e., the resonant character of the dependence of the intensity of the emission of the atomic line on the exciting-radiation wavelength, which was varied in the vicinity of the position of these absorption bands (Fig. 6b). The source of the exciting radiation in this experiment was a DKSSh-5000 lamp whose radiation was monochromatized with a DFS-12 spectrometer. The width of the excitation spectrum was 0.4 nm. When the vapor was excited by the lamp at a wavelength coinciding with the position of one of these bands ($\lambda = 714$ nm), we observed almost complete absence of emission in the molecular band $^1\Pi_u - {}^1\Sigma_g^+$ ($\lambda = 760$ nm). Only atomic fluorescence was observed with this excitation. 9) This means that the observed singularity in the absorption spectrum and in the excitation are connected with transitions of the molecules into states that lie higher than the dissociation energy of the excited molecular states, and their narrowness and intensity confirm the orbiting nature of these states.

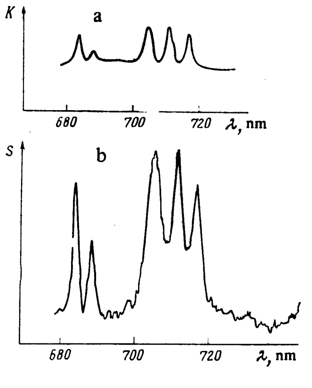

FIG. 6. Absorption spectrum (a) and excitation spectrum of the atomic lines (b) of cesium in the region 680–750 nm.

8. The considerations advanced above concerning the manifestation of orbiting states in the form of singularities in the spectra of the absorption or emission of light by the colliding atoms can be used to observe new orbiting states. It is easily understood, for example, that when two unexcited atoms collide, orbiting is possible in the ground $^1\Sigma_g^+$ state because of the binding character of this term. The orbiting parameters, calculated in analogy with the procedure described for the $^1\Pi_u$ term, turned out to be (for Cs$_2$): $r_0 = 7.1 \cdot 10^{-8}$ cm, $l_0 = 900$, $\rho = 10^{-7}$ cm, $\varepsilon_0 = 2000$ cm^{-1}. It is to be expected that the most intense transition from this orbiting state should be a transition to a bound excited state. At values $l \sim 900$, the effective potential of only one excited state $^1\Sigma_u^+$ remains binding. This circumstance is due to the large depth of the well of this state in comparison with the energy of the ground $^1\Sigma_g^+$ state. The calculated wavelength corresponding to transitions from the orbiting state $^1\Sigma_g^+$ to the state $^1\Sigma_u^+$ turned out to be $\lambda = 1180$ nm for Cs and $\lambda = 1070$ nm for Rb. The absorption spectrum of Rb and Cs vapor in this range of wavelengths was measured in[10] (Fig. 5) and it was shown that in the region adjacent to the edge of the molecular band $^1\Sigma_g^+ - {}^1\Sigma_u^+$, at high saturated-vapor temperatures, new narrow (~200–300 cm^{-1} wide) molecular bands ($\lambda = 1100$–1190 nm for Cs and $\lambda = 1000$–1080 nm for Rb) appear, and the intensity of these new bands increases with increasing temperature more strongly than the intensity of the usual molecular band $^1\Sigma_g^+ - {}^1\Sigma_u^+$ 10). The dependence of the intensity of these bands on the concentration of the atoms is close to quadratic, thus confirming the collision character of the bands in question.

The onset and the behavior singularities of the long-wave absorption bands can be explained within the framework for the proposed model as transitions from the lower orbiting $^1\Sigma_g^+$ state to an upper $^1\Sigma_u^+$ state. We note that in contrast to the previously discussed processes, in this case the two atoms are bound into a molecule only in the excited state. After the spontaneous emission of the radiation quantum at a frequency close to the excitation frequency, the produced molecule decays (owing to conservation of the orbital angular momentum) into a state of free (orbiting) atoms. It follows from the proposed model that in the case when the radiation is excited by short pulses into long-wave bands, fluorescence should be observed at the excitation wavelength, with a duration of the order of the duration of the usual molecular band. These consequences were verified experimentally by exciting Rb vapor with neodymium-laser radiation ($\lambda = 1060$ nm). An intense fluorescence was observed in this case both at the excitation wavelength and in the region of the $^1\Sigma_g^+ - {}^1\Sigma_u^+$ band. The dependence of the radiation intensity on the excitation power I_0 turned out to be different in this case: in the band at the 1060 nm wavelength it is linear up to $I_0 = 5 \times 10^4$ W/cm^2, and then increases in proportion to $\sqrt{I_0}$ (Fig. 7a), while in the band of the $^1\Sigma_g^+ - {}^1\Sigma_u^+$ transition ($\lambda = 900$ nm) it was proportional to $\sqrt{I_0}$ in the entire range of employed powers (in the latter case, the low sensitivity of the employed setup did not make it possible to measure the region of the linear dependence at low powers. According to the data of[4], the region of linear dependence appears at $I_0 < 10^3$ W/cm^2. The fluorescence-pulse duration in both bands was the same (~10^{-7}

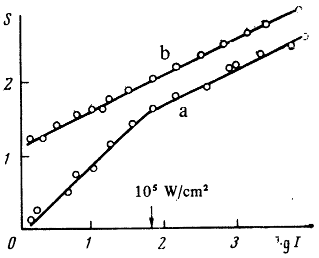

FIG. 7. Dependence of the emission of rubidium vapor: a) in the 1050 nm region; b) in the $^1\Sigma_u^+-{}^1\Sigma_g^+$ band ($\lambda = 900$ nm) on the radiation intensity I of the exciting neodymium laser.

sec) and was determined by the temporal resolution of the installation.

The observed character of the fluorescence can be explained within the framework of the proposed mechanism of formation of new bands, and contradicts the assumption that they are of intercombination origin, since the duration of the emission of these bands at the excitation frequency is of the same order as the duration of the allowed transition $^1\Sigma_g^+-{}^1\Sigma_u^+$. The large power density (compared with the ordinary molecular transitions) at which the transition takes place from the region of the linear dependence to the square-root dependence is due to the short time that the atoms stay near one another.

It should be noted in conclusion that despite the qualitative agreement obtained between the results of the proposed mechanism and the experimental data, we are far from a complete identification of the observed singularities in the absorption and emission spectra of a system of colliding atoms with the phenomenon of classical orbiting. The proposed model should be regarded only as one of the possible ones, but one that reflects well the main features of the phenomena connected with the presence of quasi-finite motions in the investigated systems.

9. On the basis of the results of our investigation we can conclude that the dynamics of atomic collisions can change substantially in the presence of a radiation field. This applies not only to the change of the energy of the translational motion of the atoms, but also to the possibility of their transition to a bound molecular state; the energy of the chemical reaction is drawn in this case from the radiation field or else is given up to the field. A study of reactions of this type may turn out to be quite interesting from the point of view of directed stimulation of chemical reactions by laser radiation.

The large effectiveness of the observed binding of the atoms may permit a substantial change in the thermodynamic equilibrium between the atomic and molecular components and a more careful investigation of the interaction between them.

The observation of quasi-finite motions in paired collisions of atoms seems particularly interesting to us. These motions correspond to specific emission (or absorption) bands of light, which are present in the spectra of the isolated atoms or molecules. An investigation of the states corresponding to these motions permits an estimate of their influence on the kinetics and on the effectiveness of the recombination processes and chemical reactions in the gas phase, and will also uncover a new possibility of obtaining stimulated emission on transition from such states in flyby molecules.

[1] In view of the low concentrations, molecule-molecule collisions have practically no effect on the processes in question.

[2] The direct proportionality of the fluorescence of the $^1\Sigma_u^+-{}^1\Sigma_g^+$ transition to $\sqrt{I_0}$ is a consequence of the molecule nonresonant excitation whose mechanism was discussed in[4].

[3] This fact was pointed out to us by S. I. Yakovlenko.

[4] At large concentrations of the Cs atoms ($\sim 10^{17}$ cm^{-3}) the molecular-fluorescence pulse contained also a longer component, the shape of which coincided with the shape of the fluorescence pulse of the Cs atoms in the D lines. The amplitude of the prolonged component did not exceed 1–10% of the amplitude of the pulse itself. The prolonged emission can be naturally attributed to excitation transfer from the atoms to the molecules.[6]

[5] The fluorescence in the D_1 line is probably due to intramultiplet transitions,[6] the manifestation of which was observed in a somewhat different kinetics of the fluorescence in the D_1 and D_2 lines.

[6] A quantum-mechanical description of "orbiting" was undertaken in[7].

[7] These estimates are only approximate for lack of exact data on the values of r_e for the molecular states of Cs_2.

[8] The cesium vapor was excited by focused laser radiation. The excitation volume was 3×10^{-3} of the total volume of the cell.

[9] The observation of emission in the 700–730 nm region was obstructed by parasitic scattering of the exciting radiation in the cell with the vapor.

[10] The new bands observed in the observation spectra were interpreted in[10] as a manifestation of intercombination transitions from the ground state $^1\Sigma_g^+$ to a bound excited triplet $3\pi_u$ state. See also[11] concerning this question.

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